Low-energy electron-impact excitation of the $\tilde{a}\,^3B_{1u}$ ($\pi\rightarrow\pi^*$) state of ethylene

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A two-state close-coupling calculation of electron-impact excitation of ethylene to the $\tilde{a}\,^3B_{1u}$ state ($\pi\rightarrow\pi^*$) is carried out using a version of the Schwinger multichannel method developed for distributed-memory parallel computers. The calculated integral cross section shows a sharp rise at threshold, in agreement with available experimental data. The integral and differential cross sections are useful in understanding the mechanism of this excitation process and indicate the possible presence of a core-excited shape resonance near threshold.

I. INTRODUCTION

One of the major hindrances to a less empirical and more robust modeling of plasmas used in materials processing—e.g., in microelectronics fabrication and surface treatment—is a lack of reliable measured or calculated cross section data for electron collisions with industrially important gases.[1] These gas-discharge plasmas are highly nonequilibrium plasmas, in which the electrons can acquire energies of tens of electron volts while the molecules remain at low temperature. The resulting electron-impact excitation, dissociation, and ionization of the gas produce reactive species which play a key role in achieving the physical and chemical modification of material exposed to the plasma.[1] Since the yield and characteristics of the desired products can be quite sensitive to the plasma operating conditions, optimization of those conditions is of economic importance. To date, optimum plasma conditions have for the most part been determined empirically, but it would clearly be desirable to predict plasma properties on the basis of microscopic processes through numerical modeling. Such modeling requires a knowledge of the cross sections for the principal collisions occurring in the plasma and on the surface, with the electron-molecule inelastic cross sections being especially important. Measurement of such cross sections is challenging, and data remain limited and fragmentary. Computational approaches to these cross sections are thus potentially very useful, provided they can deal adequately with the principal complications—such as nonspherical potentials, exchange interactions, and the role of open and closed channels—which enter into the scattering of slow electrons by molecules, in particular small polyatomics commonly used in plasma applications.[1]

Considerable progress has been made over the past decade in the *ab initio* calculation of low-energy electron-molecule collisions.[2–5] As a result, one can now calculate fairly accurate elastic cross sections for electrons colliding with diatomic as well as polyatomic targets at both the static-exchange and the static-exchange-plus-polarization levels. However, by comparison, the *ab initio* calculation of electron-impact excitation of molecules, especially of polyatomic molecules with arbitrary geometry, is still a developing field, due to its complexity and computational demands. Most methods, in practice, have been limited to diatomic or linear triatomic targets, and only recently have the Schwinger multichannel (SMC) and the complex Kohn methods been applied to polyatomic targets, water,[6] and formaldehyde,[7] respectively.

The SMC method is a general approach to electron-molecule scattering[8] and has been used to study elastic as well as inelastic collisions of electrons with both diatomic[9] and polyatomic targets.[6,10] However, the study of scattering from polyatomic targets other than small hydrides such as methane and water is a significantly more demanding task. We have recently implemented the method on distributed-memory parallel computers,[11] which for the SMC method provide higher-performance and more cost-effective computing than conventional supercomputers. Applications of this new code to elastic electron-molecule collisions at the static-exchange level have shown it capable of handling fairly large polyatomic targets.[11] We have now extended this parallel implementation to electronically inelastic collisions. As an initial application, we report here results for the ($\pi\rightarrow\pi^*$) electron-impact excitation of ethylene, leading to the $\tilde{a}\,^3B_{1u}$ state. Though relatively undemanding computationally, the calculation tests all essential aspects of the method and its implementation. Moreover, ethylene is of interest both directly, as a feed gas in plasma polymerization,[1] and as a prototype of larger hydrocarbons similarly employed.

Electronic excitation of ethylene has long been of interest to chemists. The threshold electron-impact and optical spectra have been extensively studied and summarized by Merer and Mulliken[12] and by Mulliken.[13] The ground state (N) is of ^1A_g symmetry and the $\tilde{a}$ or lowest-lying triplet state (T) is of $^3B_{1u}$ symmetry. According to experiment, this $^3B_{1u}$ state is located at about 4.6 eV vertically above the ground state, while the $^1B_{1u}$ state (V) is about 3 eV higher.

[a] Contribution No. 8501.

Both states are valence type, as has been confirmed by bound-state *ab initio* calculations.[14] Other low-lying excited states are all of Rydberg type, with the first (R) located at about 7.1 eV above the ground state. Several resonances have been seen in the threshold electron-impact spectrum. Of these, the narrow resonance at 1.8 eV and the broad resonance at 7.5 eV, both associated with the ground state, have been well studied in the early literature and more recently by Walker *et al.* in a crossed-beam experiment,[15] by Floeder *et al.* in a transmission experiment,[16] and by Sueoka and Mori using the retarding potential-time of flight (RP-TOF) method.[17] Electron-impact excitation to several Rydberg states has been studied by Trajmar *et al.*[18] Of particular interest here is the threshold excitation function of the $\tilde{X}\,^1A_g \rightarrow \tilde{a}\,^3B_{1u}$ transition, which has been measured by van Veen[19] and by Brongersma *et al.*[20] using the trapped-electron method. In the former work, a narrow feature tentatively identified as a core-excited shape resonance associated with the $^3B_{1u}$ state was observed.

Little theoretical work has been done so far for electron-ethylene scattering, although we have reported elastic cross sections obtained at the static-exchange level[11] and Schneider *et al.* have recently reported partial static-exchange-plus-polarization results.[21] Using the current implementation of the SMC method,[5,11] we have conducted further studies of electron-ethylene scattering. Results of a large-scale *ab initio* calculation of elastic electron-ethylene scattering at the static-exchange-plus-polarization level will be reported separately. In the present work, we are interested in electron-impact excitation of the $\tilde{X}\,^1A_g \rightarrow \tilde{a}\,^3B_{1u}$ transition. Since there is a large energy gap between the $^3B_{1u}$ state and other excited states, a two-state calculation, including only the $\tilde{X}$ and $\tilde{a}$ states, is expected to be quite useful. The available experimental results can be used to evaluate our theoretical method; on the other hand, the present calculation may provide some detailed scattering information which is not available experimentally, particularly the angular distributions.

In the next section the calculational procedures are given. Results and discussion are presented in Sec. III and some concluding remarks in Sec. IV.

II. CALCULATIONS

Both the formulation of the SMC method[5,8] and its parallel implementation[11] have been described previously and are here only summarized. The SMC method is a variational approximation for the scattering amplitude, in which the $(N+1)$-particle wave function is expanded in a basis and the coefficients of that expansion determined by requiring that the scattering amplitude be stationary. One of its chief advantages is that the basis set used in the expansion of the scattering wave function need not have any particular asymptotic form and may therefore be chosen for computational convenience. Specifically, in our work the $(N+1)$-electron basis functions are antisymmetrized products of Cartesian Gaussian functions; with this choice, all required matrix elements except those involving the free-particle Green's function may be evaluated analytically. A recent numerical improvement which should be emphasized here is the evaluation of the matrix elements of the projected Green's function by numerical quadrature. As shown before,[5] this modification permits converged results to be obtained using a relatively small Gaussian basis set and therefore facilitates the study of larger molecules. Each of the principal steps in the SMC method, namely the analytic evaluation of a very large set of two-electron integrals, the transformation of these integrals into matrix elements between $(N+1)$-particle functions, and the subsequent solution of a set of linear equations to obtain the scattering amplitude, is highly suited to a distributed-memory parallel implementation.[11]

The target ground state wave function was determined at the self-consistent–field (SCF) level and the experimental nuclear geometry. The Gaussian basis set used consisted of a set of valence-type functions augmented by a set of diffuse and polarization functions. The valence-type set was Dunning's $(9s5p)/[4s3p]$ for carbon and $(4s)/[3s]$ for hydrogen,[22] and the latter set is given in Table I. The diffuse functions are included to provide flexibility in representing the scattering part of the total wave function. Note that we use the full set of six Cartesian d Gaussians for each exponent, since the $x^2+y^2+z^2$ "$3s$" combination may be useful in describing the scattering wave function. The ground state SCF energy in this basis was -78.0529 a.u., compared to a near-Hartree–Fock-limit value of -78.07 a.u.[23] The same basis set and nuclear geometry were used in calculating the $^3B_{1u}$ excited state wave function, which was approximated by the improved virtual orbital (IVO) method.[24] The vertical excitation energy was 3.58 eV, in good agreement with other calculations of the same type.[14,24,25] It is known that the $^3B_{1u}$ state can be described well at the single-excitation configuration interaction (CI) or IVO level. Indeed, the value that we obtained for the perpendicular component of the expectation value of $\mathbf{r}$ in the $^3B_{1u}$ state, 12.1 a.u., is in very good agreement with the value of 12.0 a.u. obtained by McMurchie and Davidson in a converged CI calculation.[14]

All 86 virtual orbitals from the SCF calculation were used in building $(N+1)$-electron determinants. Spin-adapted combinations of these determinants were used as the trial variational functions. In particular, the "correlation terms"—that is, $\pi(\pi^*)^2$ and $\pi^2\pi^*$ configurations—needed to remove the strong orthogonality between bound and continuum orbitals were included among the trial variational functions.

We have tested the convergence with respect to both numerical quadrature and Gaussian basis set. A moderate quadrature scheme was tested first. We then doubled the

TABLE I. Exponents of diffuse and polarization Cartesian Gaussian functions for both target wave function and scattering calculations.

Center	Type	Exponents
Hydrogen	p	1.16
Carbon	s	0.0473
	p	0.0365
	d	0.8, 0.2
Center of Mass	d	0.026, 0.013

number of quadrature points and obtained results which are about 1% or less different from those in the previous case. The results presented here were obtained using the bigger quadrature scheme. Several smaller Gaussian basis sets were tried. A smaller basis set (without diffuse d functions at the center or on the carbons) which consisted of 70 contracted Gaussian type orbitals (CGTO) was tested first. This basis set gave converged results for the elastic channel at the static-exchange level but did not give converged results for electronic excitation, especially at low energies. Another basis set (with diffuse d functions on carbon but not at the center) which consisted of 82 CGTO was then tried. This basis set gave converged results for the elastic channel at both static-exchange and static-exchange-plus-polarization levels and gave fairly good results for the electronically inelastic channel. The final basis set used consisted of 94 CGTO and produced results about 5% or less different from those of the 82 function set. We thus believe that the present results are converged to within a few percent.

III. RESULTS AND DISCUSSION

The calculated excitation function (integral cross section) is plotted in Fig. 1. For comparison, the measured threshold excitation function of van Veen[19] and that of Brongersma *et al.*[20] are plotted in the same figure. Both of these measurements were made using the trapped-electron method. Note that the former, being a relative measurement, has been normalized to the theoretical maximum at 4.4 eV, and that energy above threshold is used here and elsewhere. The rapid rise of the excitation cross section near threshold, i.e., below 1.4 eV, is in qualitative agreement with both measurements, although the magnitude is different from that obtained by Brongersma *et al.* Angular-momentum analysis of the scattering amplitude, carried out by fixing the $(l,|m|)$ quantum numbers in the exit channel and summing over all l and m in the entrance channel, reveals that the threshold rise and the shoulder visible at 1.4 eV above threshold are due to a sharp peak in the $(l=2, m=\pm 1)$, or $d\pi$, contribution to the exit channel (Fig. 1, inset). This behavior is consistent with the presence of a $\pi(\pi^*)^2$ core-excited shape resonance, analogous to the π^* shape resonance in the elastic channel. The prominent peak 1.35 eV above threshold in the experimental cross section,[19] which is not seen in the calculation, has been previously interpreted by van Veen as a $\pi(\pi^*)^2$ core-excited shape resonance. Additional measurements would be very useful in clarifying the relationship, if any, between these calculated and observed features. Above 2 eV, the form of the calculated excitation function is in good agreement with the measurements of van Veen. The slow increase and decrease of the cross section around the broad peak and further monotonic decrease are characteristic features of singlet-to-triplet excitations.

To further elucidate the dynamics of this excitation, we show the differential cross section (DCS) at several energies in Figs. 2–5. The DCS at 0.4 eV above threshold is shown in Fig. 2. As mentioned above, analysis of the scattering amplitude reveals an $(l=2, m=\pm 1)$ peak centered at 1.4 eV; all other contributions are quite small near threshold. A single parity of partial wave thus dominates the exit channel at low energies, and a pattern symmetric about 90° is expected,[26] quite consistent with what is observed. At 1.4 eV (Fig. 3)

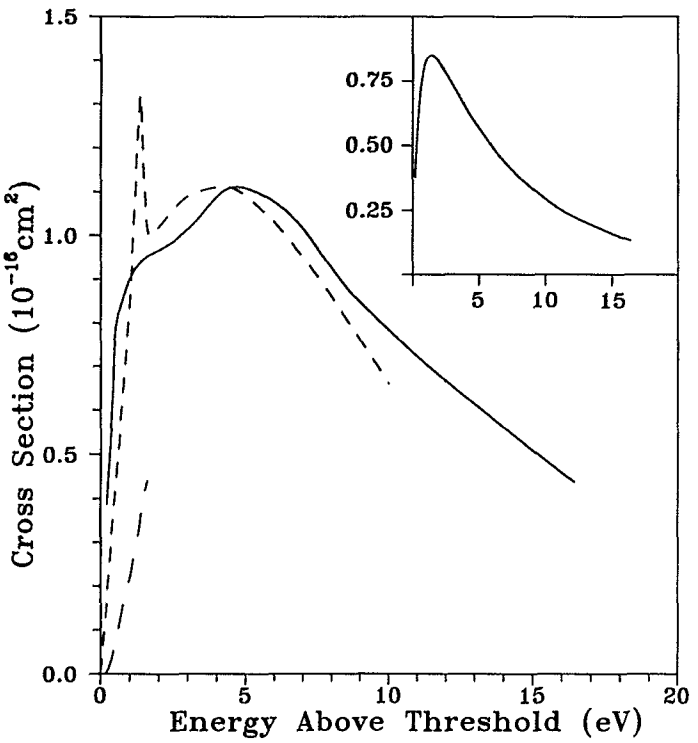

FIG. 1. Integral cross section for the $\tilde{X}\,^1A_g \rightarrow \tilde{a}\,^3B_{1u}$ electronic excitation of ethylene.—: present result; - - - -: measurement of van Veen, Ref. 19; – – –: measurement of Brongersma *et al.*, Ref. 20. Inset: ($l_{out}=2$, $m_{out}=\pm 1$) contribution to the calculated cross section.

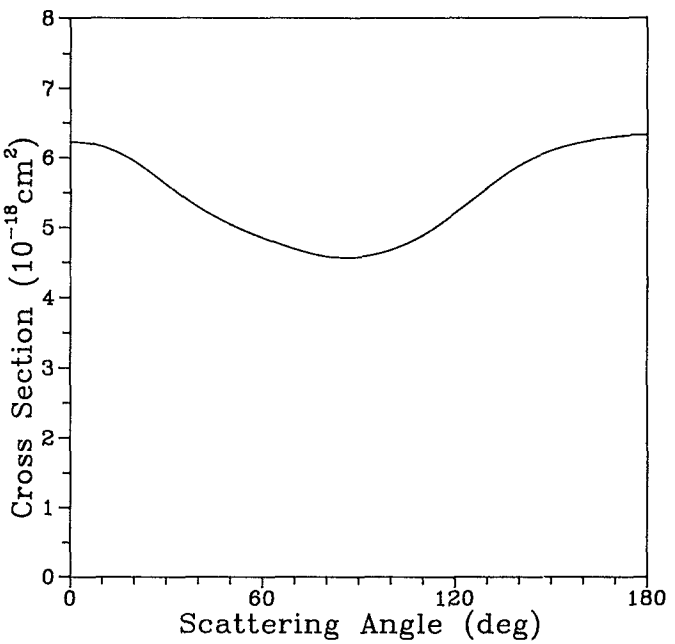

FIG. 2. Differential cross section for the $\tilde{X}\,^1A_g \rightarrow \tilde{a}\,^3B_{1u}$ electronic excitation of ethylene at 0.4 eV above threshold.

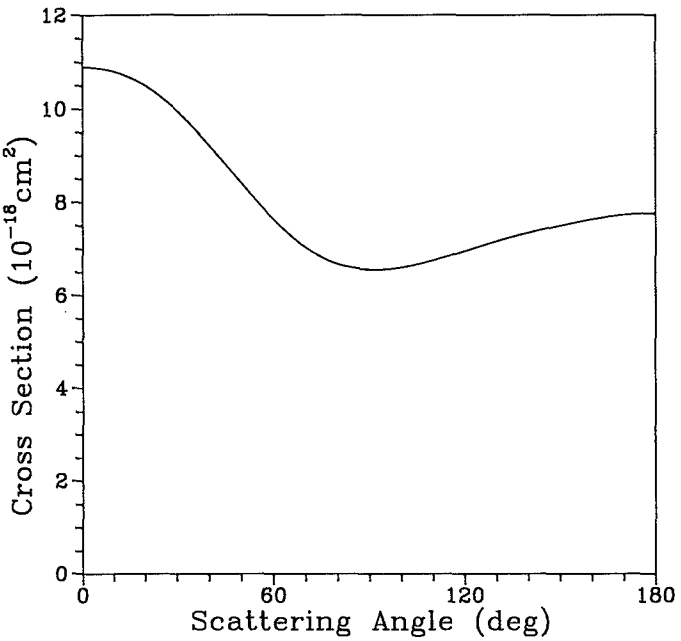

FIG. 3. Same as Fig. 2, but at 1.4 eV.

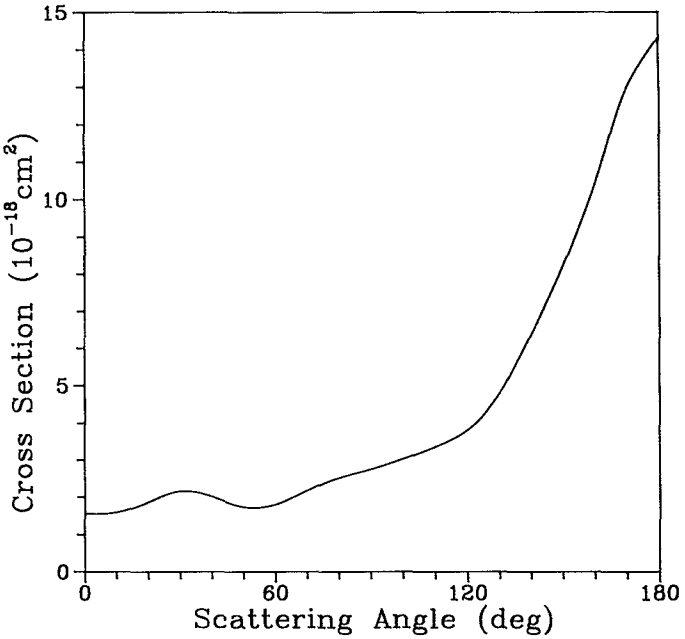

FIG. 5. Same as Fig. 2, but at 16.4 eV.

above threshold, near the maximum of the $l = 2$ contribution, the pattern is similar but somewhat less symmetric.

The DCS's at 3.4, 4.4, and 6.4 eV above threshold, covering the region of the broad maximum, are shown in Fig. 4. These show a complicated angular dependence at the lower energies. A rapidly increasing nonresonant contribution is seen at high angles, with the backward peaking characteristic of triplet excitation cross sections already pronounced at 4.4 eV.

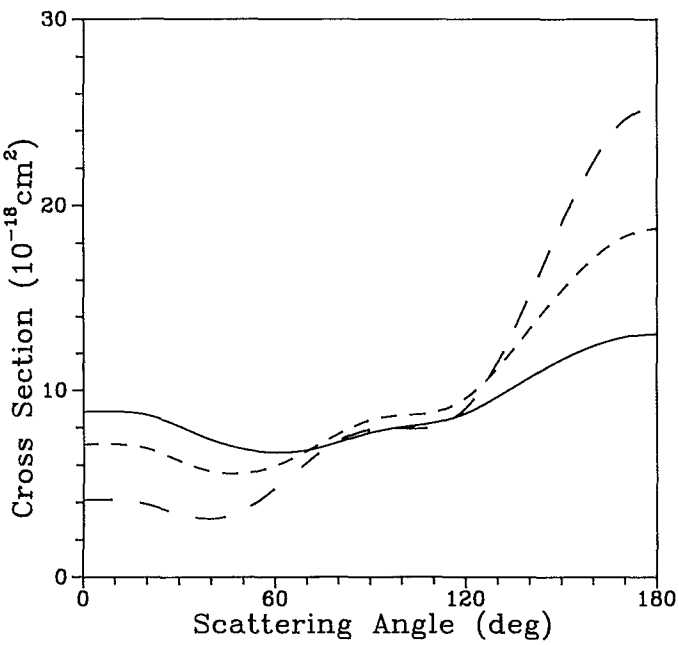

FIG. 4. Same as Fig. 2, but at 3.4 eV (—), 4.4 eV (- - - -), and 6.4 eV (– – –).

There have not yet been any direct DCS measurements for this excitation process. However, Trajmar *et al.* have measured the ratio of the ($N \rightarrow T$) DCS to that of the $\tilde{E}$ Rydberg state at 20.4 eV above the $\tilde{a}$ threshold and found that this ratio increases sharply with the scattering angle over the range 10°–80°, while the $\tilde{E}$ DCS itself decreases by about the same factor.[18] The $\tilde{a}$ state cross section should thus be slowly varying over these angles at higher energies. Our DCS at 16.4 eV (Fig. 5) shows a moderate overall increase from 10°–80°, in qualitative agreement with this conclusion.

IV. CONCLUDING REMARKS

We have applied the SMC method to the electronic excitation of C_2H_4, obtaining results in fair agreement with the limited experimental data available. Specifically, a shoulder near threshold which has the characteristics of a core-excited π^* shape resonance is observed. This shoulder causes the cross section to rise rapidly from threshold, in agreement with both experiments.[19,20] Although much less prominent, this shoulder may also be associated with the narrow feature 1.35 eV above threshold observed by van Veen.[19] At higher energies we find a broad maximum and slow decline in the cross section, again in accord with experiment. Angular distributions at low energy reflect the influence of a resonance, while at higher energies the characteristic backward peaking quickly sets in.

The present results are quite encouraging, considering the approximate nature of the calculation—e.g., use of single-configuration target wave functions, restriction to two channels, and neglect of nuclear motion—and highlight the ability of distributed-memory parallel computers to provide useful results in a cost-effective fashion. We expect to increase the cost effectiveness still further through optimization of the program, which does not yet exploit the full

potential of the newer Intel i860-based machines. On the other hand, desirable extensions of these calculations rapidly increase the computational demands. In particular, incorporation of more electronic channels may affect the cross section at higher energies; allowing for nuclear motion may also be important, since the equilibrium geometry of the $\tilde{a}$ state is quite different from that of the ground state and the electronic transition is therefore expected to be accompanied by considerable vibrational excitation. Such calculations are nonetheless quite feasible on the present generation of parallel machines, notably the 528-processor Touchstone Delta, and are planned or underway at present.

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[1]See, for example, *Plasma Reactions and Their Applications*, Japan Materials Report by Japan Technical Information Service (ASM International, Metals Park, Ohio, 1988); *Plasma Etching: An Introduction*, edited by D. M. Manos and D. L. Flamm (Academic, San Diego, 1989).
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